

T.K. Kyser · C.E. Leshner · D. Walker

The effects of liquid immiscibility and thermal diffusion on oxygen isotopes in silicate liquids

Received: 6 January 1997 / Accepted: 28 June 1998

Abstract Differences between the $\delta^{18}\text{O}$ values of Si- and Fe-rich immiscible liquids in the system $\text{Fe}_2\text{SiO}_4\text{-KAl-Si}_2\text{O}_6\text{-SiO}_2$ (Fa-Lc-Q) in isothermal experiments at 0.1 MPa have been determined experimentally to be 0.6 permil. The observed partition of ^{18}O into the Si-rich liquid is consistent with previous experience with the preferential partition of ^{18}O into Si-rich minerals in isothermal equilibrium with minerals of less polymerized structure. Crystallochemical principles affect the distribution of oxygen isotopes in coexisting isothermal liquids in the same way as they apply to isothermally coexisting crystals. The effects of Soret (thermal) diffusion on the distribution of oxygen isotopes in silicate liquids above the solvus in the system Fa-Lc-Q under conditions of an imposed temperature gradient of ca. 250 °C over 4 mm and at 2 GPa have also been investigated experimentally. Both the magnitude and the direction of separation of oxygen isotopes as a result of Soret diffusion are unexpected. For each of the silicate liquids, the cold end of the charge is enriched in ^{18}O by up to 4.7 permil, and the highest $\delta^{18}\text{O}$ values are associated with the most silica-poor compositions. The distribution of oxygen isotopes appears to be similar in each liquid, regardless of their chemical compositions, which is in contrast to the behaviour of cations whose distributions are compositionally dependent and characterized by strong crystallochemical effects wherein network-forming species such as Si and Al separate to the hot end and

Mg, Fe and Ca are segregated preferentially to the cold end. Structural units in the melts are evidently less selective between oxygen isotopes than between cations, because oxygen redistribution over all possible sites in these units proceeds according to mass. Self-diffusion coefficients of oxygen in basaltic liquids estimated from the Soret experiments are in accord with those from other isotope tracer experiments, and comparable to those of Si. The possible effects of Soret diffusion on the oxygen isotopic composition of metasomatic veins in the mantle are examined in light of these data, and indicate that decay of the thermal gradients in the veins exceeds that of the diffusion of oxygen needed to produce variations in the $\delta^{18}\text{O}$ values of mantle minerals. Variations in oxygen isotope ratios in most natural systems as a result of Soret effects are unlikely.

Introduction

Inasmuch as oxygen is the major element in natural silicate liquids, any variation in its isotopic composition normally results only from significant processes. At the high temperatures characteristic of natural silicate liquids, the fractionation of oxygen isotopes between most phases is small, normally much less than 1 permil (Taylor and Sheppard 1986; Kyser 1990). Only during processes involving two phases with distinct chemical or physical properties, such as oxides precipitating from a silicate liquid (Taylor and Epstein 1962) or CO_2 degassing from a magma (e.g. Pineau et al. 1976), will the fractionation factors for oxygen isotopes at high temperatures be great enough to effect the isotopic composition of a silicate liquid. Even then, the liquid reservoir must be extremely limited or the other phase be subtracted in substantial amount to produce any change in the isotopic composition of the liquid. As a consequence, normal magmatic processes other than extensive contamination, magma mixing or extreme fractionation should have little effect on the original oxygen isotope composition of magmas.

T.K. Kyser (✉)
Department of Geological Sciences,
Queen's University, Kingston, ON Canada, K7L 3N6;
Fax: 613 545-6592; E-mail: kyser@geol.queensu.ca

C.E. Leshner
Department of Geological Sciences,
University of California, Davis, CA 95616, USA

C.E. Leshner · D. Walker
Lamont-Doherty Geological Observatory,
Palisades, NY 10964, USA

Editorial responsibility: I.S.E. Carmichael

Two magmatic processes of limited occurrence that may result in changes of the original oxygen isotope ratios in silicate liquids are liquid immiscibility and thermal (Soret) diffusion, although the effects of these processes have not been evaluated for oxygen isotopes. In theory, liquid immiscibility could produce two liquids with slightly different oxygen isotope ratios because the extreme differences in crystallochemical properties of the two phases could proportionate oxygen isotopes differentially. On the other hand, the oxygen isotope ratios of the two immiscible liquids may not be that different because the two silicate liquids are physically and chemically similar enough to limit isotopic fractionations at the high temperatures at which silicate-liquid immiscibility occurs. Whether there are crystallochemical effects significant enough to result in different isotopic compositions between coexisting liquids is uncertain.

Soret diffusion is a disequilibrium process wherein components are redistributed in a thermal gradient. The chemical components in a silicate liquid within a thermal gradient, for example, diffuse to either the cold or hot portion of the gradient, thus resulting in chemical differentiation. This process has been studied experimentally in natural silicate liquids by Walker et al. (1981), Walker and Delong (1982), Leshner (1986) and Leshner and Walker (1986), who demonstrated that Soret effects on cation distributions are significant, and can be used to model the solution properties of silicate liquids, calculate effective binary diffusion coefficients for SiO_2 , and to proxy for element partitioning behaviour between phases in silicate melts. Although they concluded that Soret separations probably do not occur in most natural magmatic systems because thermal gradients in silicate liquids decay much faster than chemical gradients can develop, this may represent one process by which the minerals in some metasomatized mantle xenoliths have oxygen isotope ratios that are in apparent disequilibrium with other minerals (e.g. Kyser 1990). However, the magnitude of the Soret effect on oxygen isotopes in silicate liquids is not known, nor is the longevity of thermal gradients relative to rates of oxygen diffusion in metasomatic veins in the mantle.

Whether oxygen isotope ratios are affected by Soret diffusion depends on the structure of oxygen in the melt and the mechanism by which oxygen diffuses in the thermal gradient. Leshner (1986) concluded that Soret

diffusion of cations in silicate liquids is influenced primarily by their participation as network formers or modifiers, the former of which are concentrated in the hot end. Based on crystallochemical arguments, one would anticipate that ^{18}O would also segregate to the hot end because this is where Si and Al concentrate, and silicate minerals rich in these components tend to have higher $^{18}\text{O}/^{16}\text{O}$ ratios than those without network-former cations (Taylor and Epstein 1962). However, in simple gaseous and aqueous systems, thermal diffusion results in a segregation according to mass wherein the lighter species are concentrated at the hot end (Grew and Ibbes 1952). Although silicate liquids clearly are not simple systems, the diffusion of oxygen in silicate liquids may be controlled primarily by simple species (e.g. Dunn 1982), resulting in segregation of ^{16}O rather than ^{18}O to the hot end.

This study uses the results from experiments of liquid immiscibility and thermal diffusion in natural silicate liquids to characterize the magnitude of oxygen isotope fractionation associated with compositional differences and temperature gradients. Oxygen isotope fractionation by liquid immiscibility is consistent with expected crystallochemical controls. In contrast, oxygen behaves very differently than do cations in silicate liquids in a thermal gradient and this contrast reflects, in part, the different mechanisms by which species diffuse in liquids. In addition, the possible influence of thermal diffusion on the oxygen isotopic composition of minerals formed from metasomatic fluids in the mantle is examined as is the effect of immiscibility on oxygen isotope ratios. The magnitude of these effects can be substantial, but seldom will be realized in natural systems.

Experimental procedure

The effect of liquid immiscibility on oxygen isotope ratios was examined using compositions in the system $\text{Fe}_2\text{SiO}_4\text{-KAlSi}_2\text{O}_6\text{-SiO}_2$ (Fa-Lc-Q) at 1180 °C and 0.1 MPa. Samples were contained in an Fe capsule and sealed under vacuum in a silica tube. The samples were heated for 64 and 288 hours, both of which produced similar Si-rich and Fe-rich liquids (Table 1). Immiscible glasses after quench were physically separated for analysis by hand picking of fragments.

Detailed descriptions of the experimental procedures and samples for the thermal diffusion experiments are described by Walker et al. (1981) and Leshner (1986). A cylindrical furnace within

Table 1 Major element compositions and $\delta^{18}\text{O}$ values for silicate glasses from isothermal experiments at temperatures below the solvus of immiscible liquids in the system Fa-Lc-Q. Chemical compo-

sitions represent average of 10 electron-microprobe analyses of Si- and Fe-rich glasses that resulted. Initial chemical compositions are similar to those of FLQ-2 and -5 in Table 2. Pressures were 0.1 MPa

Sample	Duration (h)	Temperature (°C)		SiO_2	Al_2O_3	FeO	K_2O	$\delta^{18}\text{O}$
2LIQ-8A	64	1180	High-Si	65.9	6.7	21.0	5.4	12.6
			Low-Si	50.3	4.8	41.6	2.7	12.1
2LIQ-9A	288	1180	High-Si	66.7	6.8	21.3	5.0	12.7
			Low-Si	50.1	4.8	43.5	2.3	12.1

a 1/2-inch piston-cylinder press was used to generate thermal gradients of 60–80 °C/mm over charges 3–5 mm length. The pressures were nominally 2 GPa, the temperature difference between the ends of the charge was ca. 250 °C and the median temperature was 1425 °C. The charges contained prepared powders of either mid-ocean ridge basalt (MORB) from the Oceanographer Fracture Zone (P22), an andesite from Mount Hood (MHA) or a dacite from Mount Shasta (MSD) in a 1 mm diameter graphite capsule sealed in a Pt tube surrounded by a dry assembly of alumina (AN500), 3/8 cylindrical graphite heater, and BaCO₃ cell. Sealing in the Pt tube assured that any oxygen released from the alumina and BaCO₃ would not exchange with the liquid. The design of this system is such that extraneous sources of oxygen that would also affect the oxygen fugacity are minimal. The duration of the experiments varied between 12 and 480 hours (Table 2). The distribution of cations in the quenched glasses after the runs and the procedure for their measurement are identical to those described by Leshner (1986).

To compare the effects of thermal diffusion with those of liquid immiscibility, two thermal diffusion experiments in the system Fa-Lc-Q as described by Leshner and Walker (1986) were done at pressures of 2 GPa, mean temperatures of 1475 °C and durations of 176 and 256 hours (Table 2). The dimensions of the charges were similar to those described above for Soret diffusion experiments on igneous rocks.

The charges were cut along their length and one part mounted in epoxy, polished and analysed with SEM and electron-microprobe using the technique described by Leshner (1986). A portion of the remaining section was divided into 6–11 samples for oxygen isotope analyses, which were done using the BrF₅ procedure of Clayton and Mayeda (1963) as modified by Kyser et al. (1981). Each sample was 1–6 mg, permitting repeat isotope analyses of the majority of samples. The spatial resolution of the isotope analyses was vastly inferior to the chemical analyses obtained with the microprobe so that the concentrations for each cation in the figures represent the average over the interval used for isotope analysis. The estimated uncertainty in the isotope analyses based on repeat analyses is ± 0.3 permil. All values are reported in the familiar δ notation $\{\delta^{18}\text{O} = [(^{18}\text{O}/^{16}\text{O})_{\text{sample}} / (^{18}\text{O}/^{16}\text{O})_{\text{standard}} - 1] \times 1000\}$ in units of permil relative to VSMOW. Integrated isotopic compositions of samples were within error to those of the starting materials for all runs.

Results

Immiscibility

At temperatures within the immiscibility field of the Fa-Lc-Q system, an Si- and an Fe-rich liquid result. Differences between the $\delta^{18}\text{O}$ values of coexisting Si- and Fe-rich liquids are clearly observable at 1180 °C and are 0.5–0.6 permil, regardless of the experiments (Table 1). The Si-rich liquid is more ^{18}O -rich, as it should be, based on the relative degree of ^{18}O enrichment that correlates with Si-contents of silicate minerals.

Soret

The Soret effect is a non-equilibrium diffusion of species in response to a thermal gradient. Eventually, a steady state will be achieved wherein the tendency for chemical homogenization by diffusion of various species is balanced by thermal diffusion (Walker and DeLong 1982). The rate at which the steady state is reached depends on

the mass diffusivities of the species in that particular liquid and the length they must diffuse whereas the magnitude of the separation depends on the temperature difference and the properties of other species. As such, the time required to reach a steady state is different for each of the silicate liquids in this study because mass diffusivities for all elements vary as a function of the ratio of network formers to network modifiers (e.g. Dunn 1986). Based on observations of the rise time of the effect, from which diffusivities of SiO₂ can be calculated, Leshner and Walker (1986) determined that steady state will be achieved in ca. 150 hours for P22 (MORB) and 250 hours MHA at 1 GPa. Times in excess of 400 hours would be required for liquids having compositions equivalent to MSD and Leshner and Walker (1986) estimated that over 200 hours are required for liquids with compositions within Fa-Lc-Q.

Natural Silicate Compositions

Segregation of cations in the thermal gradient imposed on natural silicate liquids in these experiments (Figs. 1 and 2) is virtually identical to that in the more detailed study by Leshner (1986) for these liquids. The major network former, Si, segregates to the hot end of the charge, as do the alkalis, Na and K. The major network modifiers, including the alkaline earth elements, Mg and Ca, and divalent cations such as Fe, separate to the cold end of the liquid despite significant differences in the mass of these divalent cations. The Al moves with Si in mafic liquids, where the concentrations of alkalis are high enough to compensate for the charge on Al as a network former, but is segregated in the cold end with the network modifiers in more siliceous liquids. As first noted by Walker et al. (1981) and subsequently by others, Soret separation of cations in silicate liquids is not according to the mass of the cations or oxides, but rather as network-former or -modifier species.

The segregation of oxygen isotopes as a result of Soret diffusion in P22 is surprisingly marked, with the heavier species, ^{18}O , segregating with network modifiers to the cold end (Fig. 1). Comparison of the thermal diffusive profile for oxygen isotopes in P22 at different times indicates that the steady state requires time to develop, as was observed with cations (Leshner and Walker 1986). After only 12 or 65.5 hours of thermal diffusion, variations in the $\delta^{18}\text{O}$ values over the charge are not as regular as some of the cation profiles or as regular as the distribution of oxygen isotope ratios in thermal gradient over much longer periods of time (Fig. 1). The segregation of oxygen isotopes in P22 after 360 hours in the thermal gradient is regular, as would be expected in a steady state. The differences between the $\delta^{18}\text{O}$ values of the cold and hot ends after 360 hours is 4.7 permil.

Differences of several permil in $\delta^{18}\text{O}$ values between the cold and hot ends occur in all the natural silicate

Table 2 Run conditions, major element compositions and $\delta^{18}\text{O}$ values for silicate glasses from Soret experiments. Chemical compositions and temperatures represent averages of those in the samples used for oxygen isotope analyses. Detailed chemical profiles for each sample are similar to those shown in Leshner (1986)

and Leshner and Walker (1986). *P22* is a mid-ocean ridge basalt, *MHA* is an andesite from Mt. Hood, *MSD* is a dacite from Mt. Shasta, and *FLQ-2* and *-5* are glasses from liquids above the solvus in the system Fa-Lc-Q (50%B + 50%B' in Leshner and Walker 1986). Initial $\delta^{18}\text{O}$ values are shown in Figs. 1–3; $P = 2$ GPa

Sample	Duration (h)	Temperature (°C)	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	CaO	MgO	K ₂ O	Na ₂ O	$\delta^{18}\text{O}$
P22	360	1300	48.3	2.5	15.8	11.9	10.2	5.0	0.5	2.9	8.9
		1340	49.4	2.4	16.0	11.5	10.1	4.7	0.5	2.9	8.3
		1370	50.6	2.2	16.1	12.0	9.8	4.5	0.5	3.1	6.6
		1400	51.5	2.1	16.2	10.5	9.6	4.4	0.5	3.2	5.8
		1430	52.2	2.0	16.2	10.1	9.3	4.3	0.6	3.3	5.0
		1500	53.5	1.9	16.3	9.6	9.0	4.0	0.6	3.5	4.2
P22	66.5	1340	51.6	2.3	15.8	11.0	10.7	5.3	0.5	2.8	8.8
		1370	52.4	2.2	15.8	10.7	10.5	5.2	0.5	3.0	8.1
		1390	52.7	2.2	15.6	10.5	10.3	5.0	0.5	3.0	7.1
		1410	53.4	2.1	15.6	10.2	10.2	4.9	0.5	3.1	8.0
		1420	53.7	2.1	15.6	10.1	10.0	4.9	0.6	3.2	6.9
		1450	54.1	2.0	15.9	9.9	9.9	4.8	0.5	3.3	6.6
		1470	54.5	2.0	15.7	9.9	9.8	4.7	0.6	3.3	6.1
		1490	55.0	2.0	15.7	9.6	9.6	4.6	0.6	3.3	5.5
		1500	55.3	2.1	15.7	9.2	9.5	4.5	0.6	3.4	5.7
P22	12	1300	50.3	2.1	15.2	10.7	10.9	5.9	0.5	2.8	9.0
		1330	51.0	2.1	15.0	10.6	10.7	5.7	0.4	2.7	6.7
		1350	51.7	2.1	15.1	10.5	10.7	5.6	0.4	2.7	7.5
		1370	51.9	2.0	15.3	10.3	10.5	5.5	0.4	3.0	7.1
		1400	51.8	2.0	15.3	10.1	10.4	5.3	0.5	2.9	7.3
		1430	52.0	2.0	15.3	10.1	10.4	5.3	0.5	2.9	5.6
		1450	52.3	2.0	15.4	10.1	10.4	5.3	0.5	3.0	7.3
		1490	52.8	2.0	15.4	9.8	10.2	5.2	0.5	2.9	6.8
		1520	53.4	2.0	15.4	9.7	10.1	5.1	0.5	3.0	6.9
		1550	53.6	2.0	15.5	9.4	10.0	5.0	0.5	3.0	6.9
MHA	360	1300	56.9	1.1	19.0	6.9	7.0	3.5	1.0	3.9	9.0
		1360	59.6	0.9	18.9	6.0	6.4	3.1	1.1	4.2	7.5
		1380	60.1	0.9	18.5	5.6	6.0	2.8	1.1	4.5	6.9
		1400	60.9	0.8	18.2	5.1	5.7	2.6	1.2	4.4	5.7
		1430	61.7	0.8	18.0	4.8	5.4	2.5	1.3	4.5	4.8
		1470	63.8	0.7	17.7	4.4	5.0	2.2	1.4	4.5	4.4
		1500	65.5	0.6	17.1	3.8	4.5	2.0	1.4	4.7	2.2
MSD	480	1300	63.3	0.5	17.9	3.7	6.1	2.6	1.1	4.2	9.8
		1330	64.0	0.4	18.0	3.5	6.0	2.3	1.0	4.1	8.4
		1350	65.6	0.4	17.3	3.1	5.7	2.2	1.0	4.2	7.3
		1370	65.9	0.4	17.1	3.0	5.5	2.0	1.1	4.2	6.1
		1400	66.1	0.4	17.0	2.9	5.2	1.9	1.3	4.2	6.6
		1430	66.9	0.4	16.9	2.8	5.1	1.8	1.2	4.2	6.0
		1460	67.9	0.4	16.8	2.6	4.9	1.7	1.1	4.3	5.9
		1490	68.1	0.4	16.8	2.5	4.7	1.7	1.1	4.3	5.3
		1520	69.8	0.4	16.2	2.3	4.4	1.6	1.2	4.1	4.3
		1550	70.4	0.3	16.0	2.1	4.1	1.4	1.2	4.4	4.4
FLQ-2	176	1350	52.1	—	6.7	38.9	—	—	2.5	—	8.5
		1380	57.0	—	7.2	32.5	—	—	3.9	—	7.2
		1410	58.1	—	7.1	30.7	—	—	4.0	—	6.5
		1450	62.4	—	7.5	27.3	—	—	4.1	—	7.9
		1500	60.4	—	7.5	25.5	—	—	4.2	—	6.9
		1550	63.9	—	7.5	23.9	—	—	4.3	—	6.1
		1580	66.4	—	7.6	21.9	—	—	4.7	—	7.6
FLQ-5	256	1300	44.8	—	5.3	45.6	—	—	2.6	—	13.0
		1330	46.9	—	5.6	41.8	—	—	3.3	—	14.6
		1360	48.8	—	5.9	38.9	—	—	3.8	—	9.1
		1380	52.1	—	6.4	34.7	—	—	4.3	—	10.0
		1400	56.2	—	6.8	31.4	—	—	5.2	—	12.3
		1430	59.0	—	7.2	26.9	—	—	5.8	—	10.5
		1450	60.9	—	7.6	23.4	—	—	6.0	—	8.9
		1480	62.9	—	7.7	21.4	—	—	6.5	—	10.6
		1500	63.9	—	7.9	20.0	—	—	6.8	—	10.0
		1540	65.9	—	8.1	18.0	—	—	6.8	—	9.3
		1570	67.9	—	8.1	16.7	—	—	6.9	—	10.8
		1600	66.8	—	8.1	14.9	—	—	6.9	—	6.3

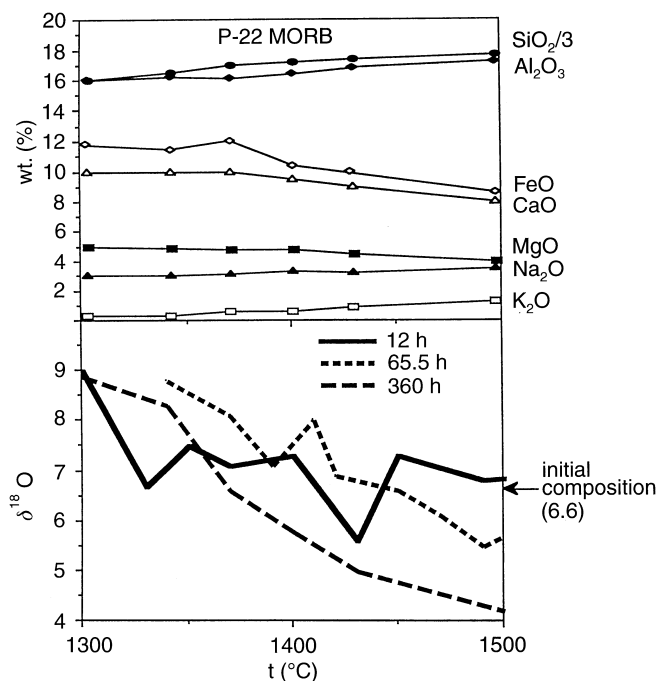


Fig. 1 Distributions of major element contents and $\delta^{18}\text{O}$ values with temperature along a thermal gradient in a mid-ocean ridge basaltic liquid (P-22). Variations in $\delta^{18}\text{O}$ values are shown for Soret experiments of different durations, and distribution of major elements are for duration of 360 hours. Also indicated is the initial $\delta^{18}\text{O}$ value of P-22. Data from Table 2

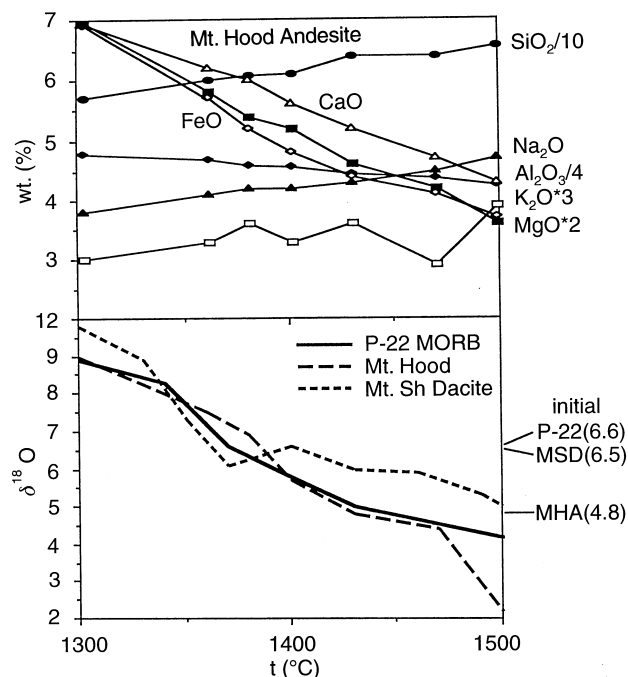


Fig. 2 Distributions of major element contents and $\delta^{18}\text{O}$ values of various silicate liquids with temperature along a thermal gradient. Also shown are the initial $\delta^{18}\text{O}$ values of the liquids. Data from Table 2

liquids, regardless of their initial isotopic or chemical compositions, or the final distribution of cations (Fig. 2). The gradients in $\delta^{18}\text{O}$ values with temperature are similar for all three natural silicate liquids, and in each ^{18}O is segregated to the cold end of the charge (Fig. 2). The regular distribution of oxygen isotopes within the thermal gradient for each composition is an indication that steady state probably was achieved.

Soret diffusion of oxygen isotopes in these natural silicate liquids differs from the Soret effect on cations in two significant ways. The magnitude of the Soret effect for oxygen isotopes is similar for silicate liquids ranging in composition from tholeiitic to dacitic. This is in marked contrast to the behaviour of cations, which segregate differentially with the composition of the liquid. In addition, oxygen isotopes segregate in the thermal gradient according to mass in that ^{18}O is at the cold end with the network modifiers, whereas ^{16}O is preferentially concentrated at the hot end with Si, the major network former. Apparently, the network-forming structural units, which migrate towards the hot end, are less selective for oxygen than for cations. The correlation between the highest $^{18}\text{O}/^{16}\text{O}$ ratios with network modifiers rather than network formers is the exact opposite of what is expected from crystallochemical behaviour of oxygen isotopes in solids.

Fa-Lc-Q compositions

Within the system $\text{Fe}_2\text{SiO}_4\text{-KAlSi}_2\text{O}_6\text{-SiO}_2$, but in a thermal gradient starting at temperatures above that of immiscibility, variations in $\delta^{18}\text{O}$ values within the thermal gradient are significantly less regular than in experiments using natural samples, although the cold end is still relatively ^{18}O -rich (Fig. 3). In contrast, the cations are regularly partitioned (Fig. 3) in the same way as the experiments with natural samples, with network formers at the hot end and network modifiers, in this case Fe, at the cold end. Irregular variations in $\delta^{18}\text{O}$ values may reflect a lack of steady state for these experiments, or more complex distribution of specific species that were slow to exchange their oxygen isotopes. The lack of achievement of steady state is plausible because the present separation took place at slightly lower mean temperature and in a significantly more Si-rich bulk composition than the experiment of Leshner and Walker (1986), which had achieved 95% of steady after 200 hours.

Leshner and Walker (1986) demonstrated that the compositional trajectories resulting from Soret separations of cations in silicate liquids within the Fa-Lc-Q system were similar to those resulting from liquid immiscibility, but this is not the case with oxygen isotopes. Oxygen isotopes are not partitioned according to crystallochemical effects in liquids above their solvus in these experiments, but segregate via Soret diffusion primarily according to mass in a thermal gradient, and secondarily by the structural components of the liquid.

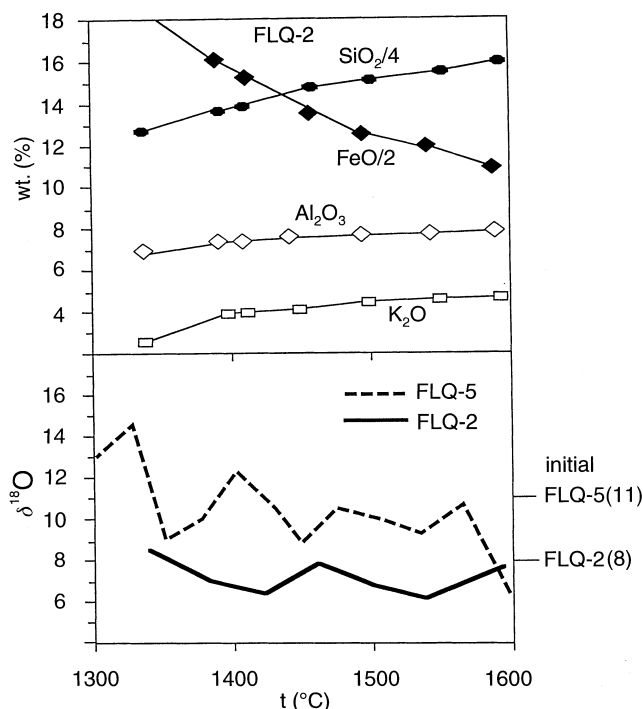


Fig. 3 Distributions of major element contents and $\delta^{18}\text{O}$ values with temperature along a thermal gradient in silicate liquids above the solvus in the system Fa-Lc-Q. Also indicated are the initial $\delta^{18}\text{O}$ values for each composition. Data from Table 2

Discussion

Prior to the advent of various techniques to determine isotopic fractionation factors between phases, Taylor and Epstein (1962) used the $\delta^{18}\text{O}$ values of coexisting natural minerals and the types of bonds within them to formulate empirical fractionations for selected minerals. Minerals with a high proportion of Si and Al in three dimensional silicate networks had the highest $\delta^{18}\text{O}$ values relative to those with cations that tend to modify this network, such that relative ^{18}O -enrichment increased with Si + Al contents of a phase in a system. These empirical observations have subsequently been verified by experimentally and theoretically determined fractionation factors between minerals (e.g. O'Neil 1986; Kyser 1987). Thus, one would predict that given two coexisting silicate liquids, the more Si-rich liquid should have the higher $\delta^{18}\text{O}$ value solely on the basis of crystallochemical effects. Indeed, this is the case for the isothermal experiments in the Fa-Lc-Q system wherein the Si-rich liquid is enriched in ^{18}O by 0.6 permil relative to the more Fe-rich liquid (Table 1). Clearly, there can be crystallochemical effects, albeit small, in silicate liquids at high temperatures.

The segregation via Soret diffusion of oxygen isotopes in silicate liquids within a thermal gradient is not influenced by the crystallochemical effects that are so prevalent in isothermal oxygen isotope distributions in silicate minerals and immiscible silicate liquids, and for

cations affected by Soret diffusion (Leshner 1986; Leshner and Walker 1986). In contrast, segregation of oxygen isotopes appears to depend only on mass, and is relatively independent of the chemical compositions of natural liquids. In fact, the Soret effect for cations in these compositions induces chemical separation gradients in the liquids which must impede the Soret separations of the oxygen isotopes observed. In the absence of these Soret-induced chemical gradients one would expect that the isotopic separations by mass, driven by thermal diffusion, would be even larger. As oxygen comprises the major part of silicate network species and cation complexes, the results from the Soret experiments indicate that the oxygen in all species in the liquid must be exchanged during diffusion. This implies that even the strongest cation-oxygen bonds must break and reform during self-diffusion of oxygen, so that oxygen can segregate according to isotopic mass rather than by crystallochemical environment. The relative ease of breaking cation-oxygen bonds during self-diffusion of oxygen in natural silicate liquids is consistent with the comparatively small activation energies recently reported for oxygen and silicon self-diffusion by Leshner et al. (in press), the results of molecular dynamics simulations (Kubicki and Lasaga 1988) and the rapid rate at which silicate species are modified in silicate liquids as measured in NMR studies (Farnan and Stebbins 1990; Stebbins et al. 1995).

Species comprised of network-forming elements, which segregate towards the hot end, should preferentially incorporate ^{18}O , at least initially. This may be why the distribution of $\delta^{18}\text{O}$ values is more random in the initial stages of Soret diffusion than is the distribution of cations. However, the equilibrium fractionation factors for oxygen isotopes among various species in the liquid are probably small, as evidenced by the results from the isothermal immiscibility experiments. Concurrent exchange of oxygen isotopes among all the various diffusing species in the liquids with segregation of ^{18}O preferentially towards the cold end must be a relatively rapid process or steady state for both cations and oxygen would not be on a comparable time scale.

Diffusivity of oxygen

Soret separation requires time to achieve steady state. The average diffusivity of a component can be calculated from Soret experiments using the rate at which the component segregates as deduced from comparison of steady state experiments with those that had not achieved steady state (Leshner and Walker 1986). The appropriate equation for the self-diffusion of oxygen from $\delta^{18}\text{O}$ values in these experiments is:

$$-\ln[1 - \Delta^{18}\text{O}_{(t)}/\Delta^{18}\text{O}_{(\text{ss})}] = tD\pi^2/d^2 \quad (1)$$

where $\Delta^{18}\text{O}$ is the difference between the $\delta^{18}\text{O}$ values of the cold and hot ends from experiments at some time (t) before steady state is achieved relative to the differences

at steady state (ss), and D is the tracer diffusion coefficient. The steady state values can be found by equating the left side of Eq. (1) for two separate times and solving for D and $\Delta^{18}\text{O}_{(\text{ss})}$. Using the results from the three experiments with P22 (MORB), $D_{\text{Oxygen}} = 3.4 \times 10^{-7} \text{ cm}^2/\text{sec}$ (Fig. 4). This value is slightly lower than the effective binary diffusion coefficient for SiO_2 in P22 ($3.05 \times 10^{-7} \text{ cm}^2/\text{sec}$; Leshner and Walker 1986), as would be expected if diffusion of oxygen were a cooperative process with network cations, and rate-limited by the formation of high-coordinated Si (and Al) transition complexes (e.g. Angell et al. 1982; Liu et al. 1988). This measure of the self-diffusion coefficient represents the average diffusivity of oxygen at a mean temperature of 1425°C because the actual value changes over the length of the charges as the temperature changes. Nevertheless, this determination is indistinguishable from the self-diffusion coefficients for oxygen and silicon determined by Leshner et al. (in press) for basaltic melt at 1400°C and 2 GPa. Self-diffusion coefficients for oxygen in the other Soret experiments, which presumably are lower as the liquids become more siliceous and viscous (e.g. Muehlenbachs and Kushiro 1974; Oishi et al. 1975; Leshner and Walker 1986; Canil and Muehlenbachs 1990), cannot be calculated, but the mechanism by which oxygen isotopes diffuse in these must be similar to that in the P22 liquid because the segregation profiles are similar.

Although there are numerous diffusion studies for cations in natural silicate liquids, those for oxygen are limited. Many of the measurements of oxygen diffusion in melts have used the oxidation or reduction of Fe in the liquid to trace the movement of oxygen through the liquid, which is a chemical diffusivity (e.g. Dunn 1983; Wendlandt 1991). During the reduction process, either oxygen anions (Dunn 1983), neutral species or electrons (Wendlandt 1991) may be the diffusing species. Few have determined self-diffusion coefficients for natural melts, which are most analogous to those from the Soret separations.

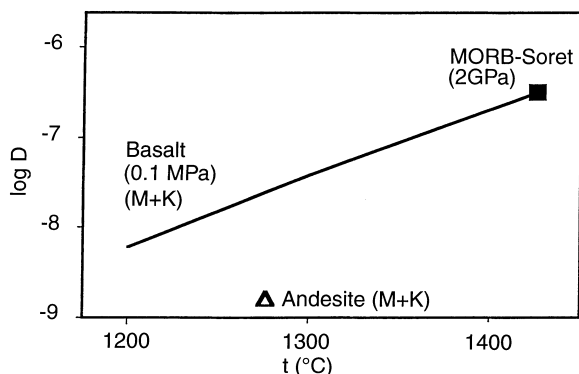


Fig. 4 Diffusivities of oxygen in silicate liquids of P22 (square, MORB-Soret) deduced from Soret experiments at 2 GPa in this study relative to those measured at various temperature and 0.1 MPa by Muehlenbachs and Kushiro (1974) for basalt (line) and andesite (triangle)

Muehlenbachs and Kushiro (1974) traced the diffusion of oxygen isotopes using a liquid-gas technique in basaltic and andesitic liquids between 1280 and 1530°C and 0.1 MPa pressure, and suggested a value at 1425°C of $D_{\text{Oxygen}} = 3.1 \times 10^{-7} \text{ cm}^2/\text{sec}$ for self-diffusion of oxygen in basaltic liquid, consistent with the value from the Soret experiments (Fig. 4). Canil and Muehlenbachs (1990) reported a slightly lower self-diffusion coefficient of oxygen in an Fe-Ti basalt at 1425°C and 0.1 MPa.

The diffusivities for oxygen in P22 are similar to the major cation, Si, in the Soret experiments, consistent with complex anion species affecting the diffusivities of oxygen. Oxygen isotope ratios in silicate liquids within the Fa-Lc-Q system do not change regularly along the thermal gradient, but cation concentrations do, although somewhat less regularly than in natural silicate liquids (Fig. 3). Leshner and Walker (1986) suggested that Soret separation of cations resembles that of cation segregation in equilibrium liquid immiscibility. In contrast, oxygen isotopes in silicate liquids within the Fa-Lc-Q system are segregated more or less according to mass, but the irregular distribution of $\delta^{18}\text{O}$ values with thermal gradient indicates the process is more complex than in other silicate liquids. The $\delta^{18}\text{O}$ profiles do not represent steady state, although Leshner and Walker (1986) have suggested that similar distributions of highly mobile cations ($D_{\text{cation}} \gg D_{\text{SiO}_2}$) in this system probably do. In contrast to cations, slower exchange of oxygen among complex anionic species in these immiscible liquids as a result of competing crystallochemical effects in these highly non-ideal liquids may contribute to the irregular distribution of $\delta^{18}\text{O}$ values.

Application to mantle metasomatism

Soret diffusion could theoretically result in significant variations in the $\delta^{18}\text{O}$ values of silicate liquids if a thermal gradient can be maintained. One such high-temperature environment where small but significant variations in the $\delta^{18}\text{O}$ values of minerals associated with silicate liquids occur is in mantle xenoliths hosting metasomatic veins (Kyser 1990). A few mantle xenoliths have significantly different $\delta^{18}\text{O}$ values (i.e. 0.5–1 permil) within, and proximal to, veins of minerals that either precipitated from a silicate liquid or formed by reaction between the liquid and the host mantle (Kyser 1990). The origin of such variations in the $\delta^{18}\text{O}$ values of mantle xenoliths remains controversial (e.g. Gregory and Taylor 1986; Kyser 1990; Matthey et al. 1994). The extreme segregation of oxygen isotopes as a result of Soret diffusion realized in this study may deserve a cursory evaluation as a mechanism to produce these variations. A thermal gradient will be induced if a metasomatic silicate liquid at ca. 1300°C and having a $\delta^{18}\text{O}$ value of 4.5 enters a depleted portion of the mantle at 1200°C and having a $\delta^{18}\text{O}$ value of 6.5 as shown in Fig. 5a. These $\delta^{18}\text{O}$ values represent extremes in mantle minerals (Kyser 1990). Any Soret effect should result in

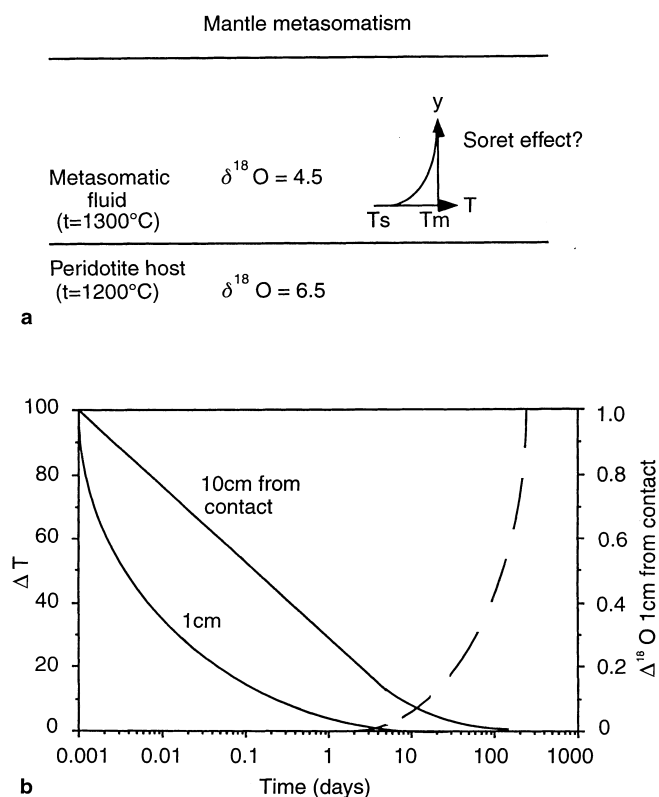


Fig. 5 **a** Schematic diagram of initial $\delta^{18}\text{O}$ values, temperatures and temperature profile with distance y in a metasomatic fluid invading a peridotite host in the mantle. T_s is the temperature of the solid and T_m is the temperature of the metasomatic fluid. **b** Calculated differences in the temperatures (ΔT) and $\delta^{18}\text{O}$ values ($\Delta^{18}\text{O}$) with time in a metasomatic fluid after it has invaded a mantle host as shown in **a**. Temperature differences in the fluid with time are for 1 and 10 cm from the contact between the metasomatic fluid and the host (as labelled), and for 1 cm from the contact for the $\delta^{18}\text{O}$ values (dashed)

liquids (or minerals from them) in the centre of the vein that have much lower $\delta^{18}\text{O}$ values than the initial liquid because ^{18}O should segregate to the host-liquid interface. The decay of the thermal gradient can be modelled assuming moderate thermal conductivities of $k = 10^{-2} \text{ cm}^2/\text{sec}$ and the following relations:

$$(T - T_o)/(T_s - T_o) = \text{erfc}[y/2(kt)^{1/2}] \quad (2)$$

where T is the temperature in the liquid a distance (y) after a time (t), T_o is the original temperature of the liquid and T_s is the temperature at the interface, taken to be 1200 °C. Substitution of the diffusivity for oxygen from Muehlenbachs and Kushiro (1974) at 1300 °C for k in Eq. 2 results in a similar equation for the change in the $\delta^{18}\text{O}$ values of the liquid. Calculated changes in the thermal and isotopic gradients with time are shown in Fig. 5b as the decay of the thermal gradient with time at 1 cm and 10 cm from the interface and the relative change in $\delta^{18}\text{O}$ value of the liquid 1 cm from the interface. The decay of the thermal gradient even 10 cm from the interface occurs faster than oxygen isotopes can segregate as a result of the Soret effect. The varia-

tions in $\delta^{18}\text{O}$ values that occur in some mantle xenoliths remain enigmatic. Given the much faster rates of diffusion of heat relative to mass (Walker and Delong 1982; Leshner 1986), Soret effects on the oxygen isotopic composition of most natural systems will be limited at any scale.

Concluding remarks

Soret, or thermal, diffusion produces variations of several permil in the distribution of oxygen isotope ratios in natural silicate liquids within extreme temperature gradients of ca. 250 °C/4 mm. Isotopes of oxygen are segregated in such gradients according to mass, wherein ^{18}O accumulates preferentially at the cold end with network-modifying cations such as Mg, Fe and Ca. Lower $\delta^{18}\text{O}$ values in the most Si-rich portions of silicate liquids is the opposite of what is expected from the crystallochemical effects observed on the $\delta^{18}\text{O}$ values of immiscible silicate liquids in the system Fa-Lc-Q, in which the Si-rich liquid is 0.6 permil higher than the coexisting Fe-rich liquid. In addition, the segregation of oxygen isotopes by mass rather than by crystallochemical effects that determine cation distributions in silicate liquids in a thermal gradient indicates that isotopic exchange of oxygen among complex anionic species occurs during self-diffusion of oxygen.

Diffusivities of oxygen deduced from Soret experiments on a natural basaltic liquid are comparable to those of Si estimated from previous Soret experiments. The time required to reach steady state for oxygen isotope ratios in Soret diffusion experiments varies with composition of the silicate liquid, but the magnitude of the separation of oxygen isotopes appears to be compositionally independent. These data, in conjunction with similar diffusivities for oxygen and Si, suggest that oxygen diffusion occurs via exchange among complex species, thus requiring the breaking and forming of even the strongest cation-oxygen bonds. Regardless of the exact mechanism by which oxygen diffuses through silicate liquids, the diffusivities deduced from the Soret experiments indicate that the small but significant variations in the $\delta^{18}\text{O}$ values of mantle minerals, or in most other natural systems, are unlikely to result from Soret effects because of the rapid decay of the thermal gradients needed to promote Soret diffusion.

Acknowledgements This manuscript benefitted greatly from a review by Karlis Muehlenbachs. Funds for this research were primarily from NSERC and NSF grants to the authors.

References

- Angell CA, Cheeseman PA, Tamaddon S (1982) Pressure enhancement of ion mobilities in liquid silicates from computer simulation studies to 800 kilobars. *Science* 218: 885–887
- Canil D, Muehlenbachs K (1990) Oxygen diffusion in an Fe-rich basalt melt. *Geochim Cosmochim Acta* 54: 2947–2951

- Clayton RN, Mayeda TK (1963) The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analysis. *Geochim Cosmochim Acta* 27: 43–52
- Dunn T (1982) Oxygen diffusion in three silicate melts along the join diopside-anorthite. *Geochim Cosmochim Acta* 46: 2293–2299
- Dunn T (1983) Oxygen chemical diffusion in three basaltic liquids at elevated temperatures and pressures. *Geochim Cosmochim Acta* 47: 1923–1930
- Dunn T (1986) Diffusion in silicate melts. In: Scarfe CM (ed) Short course in silicate melts, 12. Mineral Assoc Can, Ottawa, pp 57–92
- Farnan I, Stebbins JF (1990) High-temperature ^{29}Si NMR investigation of solid and molten silicates. *J Am Chem Soc* 112: 32–39
- Gregory RT, Taylor HP (1986) Non-equilibrium, metasomatic $^{18}\text{O}/^{16}\text{O}$ effects in upper mantle mineral assemblages. *Contrib Mineral Petrol* 93: 124–135
- Grew KE, Ibbs TL (1952) Thermal diffusion in gases. Cambridge Univ Press, NY
- Kubicki JD, Lasaga AC (1988) Molecular dynamics simulations of SiO_2 melt and glass: ionic and covalent models. *Am Mineral* 73: 941–955
- Kyser TK (1987) Equilibrium fractionation factors for stable isotopes. In: Kyser TK (ed) Short course in stable isotope geochemistry of low temperature fluids, 13. Mineral Assoc Can, pp 1–84
- Kyser TK (1990) Stable isotopes in the continental lithospheric mantle. In: Menzies M (ed) The continental lithospheric mantle. Oxford University Press, NY, pp 127–156
- Kyser TK, O'Neil JR, Carmichael ISE (1981) Oxygen isotope thermometry of basic lavas and mantle nodules. *Contrib Mineral Petrol* 77: 11–23
- Leshner CE (1986) Effects of silicate liquid composition on mineral-liquid element partitioning from Soret diffusion studies. *J Geophys Res* B6: 6123–6141
- Leshner CE, Walker D (1986) Solution properties of silicate liquids from thermal diffusion experiments. *Geochim Cosmochim Acta* 50: 1397–1411
- Leshner CE, Hervig RL, Tinker D (1998) Self diffusion of network formers (silicon and oxygen) in naturally occurring basaltic liquid. *Geochim Cosmochim Acta* (in press)
- Liu S-B, Stebbins JF, Schneider E, Pines A (1988) Diffusive motion in alkali silicate melts: an NMR study at high temperatures. *Geochim Cosmochim Acta* 52: 527–538
- Mattey DP, Lowry D, Macpherson CG (1994) Oxygen isotope composition of mantle peridotite. *Earth Planet Sci Lett* 128: 231–241
- Muehlenbachs K, Kushiro I (1974) Oxygen isotope exchange and equilibration of silicates with CO_2 and O_2 . *Carnegie Inst Washington* 73: 232–236
- O'Neil JR (1986) Theoretical and experimental aspects of isotope fractionations. In: Valley JW, Taylor HP, O'Neil JR (eds) Stable isotopes in high temperature geological processes. (Reviews in mineralogy, 16) Mineral Soc Am, Washington, DC, pp 1–37
- Oishi Y, Terai R, Ueda H (1975) Oxygen diffusion in liquid silicates and relation to their viscosity. In: Cooper AR, Heuer AH (eds) Mass transport phenomena in ceramics. Plenum Press, NY, 297–310
- Pineau F, Javoy M, Bottinga Y (1976) $^{13}\text{C}/^{12}\text{C}$ ratios of rocks and inclusions in popping rocks of the Mid-Atlantic ridge and their bearing on the problem of deep-seated carbon. *Earth Planet Sci Lett* 29: 413–421
- Stebbins JF, Sen S, Farnan I (1995) Silicate species exchange, viscosity and crystallization in a low-silica melt: in situ high-temperature MAS NMR spectroscopy. *Am Mineral* 80: 861–864
- Taylor HP, Epstein S (1962) Relationship between $^{18}\text{O}/^{16}\text{O}$ ratios in coexisting minerals of igneous and metamorphic rocks, part I. *Geol Soc Am Bull* 73: 461–480
- Taylor HP, Sheppard SMF (1986) Igneous rocks. I. Processes of isotopic fractionation and isotope systematics. In: Valley JW, Taylor HP, O'Neil JR (eds) Stable isotopes in high temperature geological processes. (Reviews in Mineralogy, 16) Mineral Soc Am, Washington, DC, pp 227–272
- Walker D, DeLong SE (1982) Soret separation of mid-ocean ridge basalt magma. *Contrib Mineral Petrol* 79: 231–240
- Walker D, Leshner CE, Hays JF (1981) Soret separation of lunar liquid. *Proc Lunar Planet Sci* 12B: 991–999
- Wendlandt RF (1991) Oxygen diffusion in basalt and andesite melts: experimental results and discussion of chemical versus tracer diffusion. *Contrib Mineral Petrol* 108: 463–471